

CITRUS SCIENCE AND TECHNOLOGY

Volume 1
Nutrition, Anatomy, Chemical Composition
and Bioregulation

Edited by: STEVEN NAGY, Ph.D.

*Research Chemist
U.S. Citrus and Subtropical
Products Laboratory
Southern Region, Florida
Antilles Area, USDA, ARS
Winter Haven, Florida*

PHILIP E. SHAW, Ph.D.

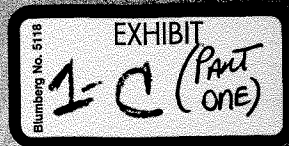
*Research Leader
U.S. Citrus and Subtropical
Products Laboratory
Southern Region, Florida
Antilles Area, USDA, ARS
Winter Haven, Florida*

MATTHEW K. VELDHUIS, Ph.D.

*Formerly Laboratory Chief
U.S. Citrus and Subtropical
Products Laboratory
Southern Region, Florida
Antilles Area, USDA, ARS
Winter Haven, Florida*

THE AVI PUBLISHING COMPANY, INC.
WESTPORT, CONNECTICUT

13807



1973. IDENTIFICATION OF 2,4,6-trihydroxyacetophenone. *J. Agric. Food Chem.* 21, 738-739. Six new flavonoids from citrus. *Phytochemistry* 12, 1001-1004.

oranges. 1. Hydrocarbons. Identified by gas chromatography and mass spectra. *J. Food Sci.* 28, 1001-1004.

DEL, P., and BUCHI, G. 1968. The occurrence of a natural antioxidant in citrus fruits. *Phytochemistry* 7, 928.

and KROTORA, G. I. 1971. Hydrocarbons in citrus flower. *Tr. Gruz. Nauch. Issled. Obshch.* 78, 47641k).

could become important profit item.

tangerine juices. In *Fruit and Vegetable Processing*. D. K. Tressler, and M. A. Joslyn, Eds. Conn. Agric. Expt. Sta. Bull. 697.

water-soluble aromatics distilled from citrus fruits. *J. Food Sci.* 37, 108-112.

K. 1968. Nomenclature of ylangene, geranyl acetate, and limonene. *J. Food Sci.* 33, 697.

limonene and its derivatives. Part II. *J. Food Sci.* 33, 877-886.

content of Florida citrus essential oils. *J. Food Sci.* 33, 877-886.

and BRADDOCK, R. J. 1976. Method for the determination of citrus essential oils. *J. Food Sci.* 51, 129-132.

Florida lemons in frozen concentrate for processing. *J. Food Sci.* 51, 129-132.

limonene. *Arkiv. Kemi.* 11, 211-218.

published observations.

on of citrus species and varieties by *Proc. Am. Soc. Hort. Sci.* 84, 204-205.

and ATTAWAY, J. A. 1971. Physicochemical properties of citrus essential oils from Florida. *J. Agric. Food Chem.* 19, 1001-1004.

d odor thresholds and interactions of citrus essential oils. *J. Food Sci.* 33, 877-886.

Thesis, Univ. of Florida, Gainesville.

citrus oils. *Flavour Ind.* 647-653.

Philip E. Shaw

Aqueous Essences

Citrus essences are distilled aqueous solutions of the more volatile components from the corresponding citrus juices. Commercially they are added to concentrated citrus juices to impart fresh fruit flavor that was lost during the concentration process and not restored by addition of peel oil and cut-back juice. Essence may be collected from fresh juice either by partial distillation prior to juice evaporation or by condensation of volatiles from the early stages of evaporation (Wolford *et al.* 1969).

The full commercial potential of essence has not been realized as yet because of the difficulty in obtaining a standardized product. The strength and flavor characteristics of essences vary with the type of evaporator employed, cultivar, season of harvest, rootstock and horticultural practices; but variations can be minimized by blending essences (Veldhuis 1971). Many chemical methods for evaluation of essence strength and quality have been developed in an effort to provide standardized essence solutions. However, subjective organoleptic evaluation is still necessary to adequately evaluate essence for satisfactory use in flavoring citrus products (Wolford *et al.* 1969).

Orange essence is widely used as a flavoring component in frozen concentrated orange juice and in partially synthetic frozen concentrated orange drinks where its storage stability for up to 30 months in these products has been demonstrated (Dougherty *et al.* 1974). Grapefruit essence is used in some frozen concentrated grapefruit juice packs, and lemon essence is used as a citrus flavoring agent. However, tangerine and lime essences have not as yet been widely used commercially to flavor citrus products. Of the five citrus essences the aromas of lemon and lime essence most resemble the fruit from which they were produced.

ORANGE ESSENCE

Qualitative Composition

Many studies have been carried out to determine the qualitative composition of orange essence, but there have been few comparable studies on other citrus essences. Because orange essence is widely used commercially in frozen concentrated orange juice, its composi-

tion has been of considerable interest to the citrus industry. In addition, those engaged in citrus flavor research have felt that analysis of orange essence might result in an understanding of the components necessary to create a fresh orange flavor. Earlier studies on orange oil and other orange flavor fractions had suggested certain components as important to orange flavor, but had not yielded a single compound or group of compounds responsible for the full, delicate and complex flavor of orange.

Orange essence contains compounds also found in other orange flavor fractions. Since orange juice contains some peel oil, volatile components are partitioned between juice and peel oil. Distillation of juice to produce aqueous essence also affords an oily layer called essence oil that must be separated before aqueous essence can be utilized. Thus, many of the same components have been identified in essence, peel oil and essence oil (Veldhuis 1971).

The 142 components of orange essence that have so far been identified are listed in Table 12.1. Nineteen separate studies on aqueous orange volatiles have been reviewed in compiling this list. Footnotes to each compound indicate who reported the compound and the number of times each has been identified as an orange essence component. Although most of the compounds listed were not found in any one study, most were identified more than once as an essence constituent. In all but two cases analyses were performed on aqueous essences distilled in the laboratory or prepared commercially. Although aqueous essence was not produced in the other two studies, orange juice volatiles in the gas phase were swept from the juice and collected for subsequent analysis. Thus, Schultz *et al.* (1971) used a trap packed with an organic-polymer material (e.g., Chromosorb 101) in which organic volatiles from the headspace of orange juice were more strongly absorbed than water vapor. An anhydrous mixture of organic components was released from the trap by heat. Dinsmore and Nagy (1971) bubbled nitrogen through orange juice so that the volatiles were swept through a dinitrophenylhydrazine solution. The volatile carbonyls were trapped as dinitrophenylhydrazones and then regenerated for gas chromatographic separation. Except for the two early studies of Hall and Wilson (1925) and Kirchner and Miller (1957), individual components were generally isolated by gas chromatography and identified by retention time and infrared spectroscopy and/or mass spectrometry. In one study 68 essence components were identified from more than 200 separated by a capillary column and detected by an electron capture detector (Wolford and Attaway 1967).

Ten organic acids have been identified in orange essence and special

TABLE 12.1
ORANGE ESSENCE COMPOSITION

Acids	
Acetic acid ¹⁻⁴	
Butyric acid ^{1,3,4}	
Decanoic [capric] acid ^{4,1,3}	
Formic acid ^{1,3-5}	
Hexanoic acid ^{1,3,4}	
3-Methylbutanoic [isovaleric] acid ^{1,3}	
(4-Methylpentanoic [isocaproic] acid) ^{1,3}	
Octanoic acid ^{1,3,4}	
Pentanoic [valeric] acid ^{1,3}	
Propionic acid ^{1,3,4}	
Alcohols	
1-Butanol ^{1,3,4,6-9,18}	
2-Butanol ³	
<i>cis</i> -Carveol ¹⁰	
<i>trans</i> -Carveol ^{1,3,4,6,8-11}	
Citronellol ^{1,3,4,8,9,11-15}	
1-Decanol ^{1,3,4,8,9}	
Ethanol ^{1-11,13,14,18}	
Geraniol ^{1,3-5,8,9,11,12,14}	
Heptanol ^{10,18}	
3-Hepten-1-ol ^{3,9,14}	
1-Hexanol ^{1,3,4,6-13,18}	
2-Hexanol ¹⁴	
<i>trans</i> -2-Hexen-1-ol ^{6,13}	
<i>cis</i> -3-Hexen-1-ol ^{1,3,4,6,8-13,18}	
Isohexanol ¹	
Linalool ^{1,3,4,6,8-13,15,18}	
<i>cis</i> -2,8-p-Menthadiene-1-ol ¹⁰	
<i>trans</i> -2,8-p-Menthadiene-1-ol ^{10,12}	
1,8-p-Menthadiene-9-ol ^{10,12}	
8-p-Menthadiene-1,2-diol ¹²	
Methanol ^{1,3,6-11,14}	
2-Methyl-1-butanol ⁷	
3-Methyl-1-butanol [isopentanol] ^{1,4,6,7,9,10,13}	
2-Methyl-3-butanol ^{2,10,13}	
Methyl heptenol ^{1,3,4,11}	
2-Methyl-1-propanol [isobutanol] ^{1,4,6,7,9,10,18}	
Nerol ^{1,3,4,8-11,14}	
1-Nonanol ^{1,3,4,8,9,11}	
2-Nonanol ^{1,8,11}	
1-Octanol ^{1,3,4,6,8-13}	
1-Pentanol ^{1,3,4,8,9,11}	
2-Pentanol ³	
1-Penten-3-ol ^{6,10,18}	
2-Phenyl ethanol ⁵	
1-Propanol ^{1,3,4,6,7,9,11,13}	
Terpinen-4-ol ^{1,3,4,6,9-14}	
α -Terpineol ^{1,3-6,8-15}	
Aldehydes	
Acetaldehyde ^{2,3,5-8,10,11,13,14,16-18}	
Benzaldehyde ^{6,7}	
Butyraldehyde ^{13,17}	
Citronellal ^{3,4,6,8,9,14,15}	
Decanal ^{3,4,6,8,9,11,13-15,18}	
3-Ethoxyhexanal ¹⁸	
α -Ethylbutyraldehyde ^{3,8,11,14}	
2-Ethyl hexanal ¹⁴	
Furfural ^{2,11,14,16}	

(continued)

TABLE 12.1 (Continued)

Geraniol ^{3,4,6,8,9,11,12,14,16}
Hexanal ^{3,7-16,18}
2-Hexenal ^{3,4,6-12,14-16}
Malonaldehyde ¹⁹
Neral ^{3,4,6,8-12,14,16}
Nonanal ^{1,3,4,8,9,11,14,15,18}
Octanal ^{3,4,6-12,14-16,18}
2-Octenal ^{3,8,11,16}
<i>trans</i> -2-Pentenal ¹⁰
Perillaldehyde ^{9,10,13}
Propionaldehyde ¹⁸
Undecanal ^{3,8,9,11,14}
Esters
Butyl butyrate ⁴
Citronellyl acetate ¹⁴
Citronellyl butyrate ^{3,4}
Ethyl acetate ^{5-8,10,11,13,18}
Ethyl butyrate ^{3,4,6,7,9-14,18}
Ethyl decanoate ^{3,4}
Ethyl formate ^{5,11,13,14,18}
Ethyl hexanoate ^{6,13}
Ethyl 3-hydroxyhexanoate ^{6,12,13}
Ethyl isobutyrate ⁷
Ethyl octanoate ^{3-6,8,9,11,13,14}
Ethyl 2-methylbutyrate ⁷
Ethyl propionate ^{3,7,10}
Linyl acetate ^{3,4}
Methyl butyrate ^{6,7,10,12,18}
Methyl hexanoate ^{6,7}
Methyl 3-hydroxyhexanoate ¹³
Methyl <i>N</i> -methylanthranilate ^{8,11,14}
(Methyl 3-methylbutyrate [isovalerate]) ¹¹
Methyl octanoate ¹⁴
Octyl acetate ^{9,13}
Octyl butyrate ^{11,14}
Octyl 3-methylbutyrate [isovalerate] ¹¹
Terpinyl acetate ^{8,11,14}
Terpinyl formate ^{3,4}
Hydrocarbons
Benzene ^{b,13,18}
Biphenyl ^{b,6,13}
Δ^3 -Carene ^{3,8,9,11}
Carvophyllene ⁶
Cyclohexane ^{b,13}
<i>p</i> -Cymene ^{3,4,8,11,14}
Ethyl benzene ^{b,13}
Hexane ^{b,13}
<i>p</i> -Isopropenyl toluene ¹³
<i>d</i> -Limonene ^{3,4,6-15,18}
Methane ^{b,13}
Methyl cyclopentane ^{b,13}
2-Methylpentane ^{b,13}
3-Methylpentane ^{b,13}
Myrcene ^{3,4,6-9,11,13-15,18}
α -Phellandrene ³
β -Phellandrene ³
α -Pinene ^{3,4,7-9,11,14,15,18}
β -Pinene ^{3,4,9,14,18}
γ -Terpinene ^{3,8,11}
γ -Terpinene ^{3,4,7-9,11}
Terpinolene ^{3,7,8,11}
α -Thujene ⁷

TABLE 12.1 (Continued)

Toluene ^{b,13}
Valencene ^{6,14,15,18}
<i>o</i> -Xylene ^{b,13}
<i>m</i> - or <i>p</i> -Xylene ^{b,13}
Ketones
Acetone ^{2,3,5,8-14,17}
Butanone ^{13,17}
Carvone ^{3,4,6,8-16}
Methyl heptenone ^{3,4,9}
4-Methyl-2-pentanone ¹³
Nootkatone ¹³
2-Octanone ⁸
2-Pentanone ^{7,17}
1-Penten-3-one [ethyl vinyl ketone] ¹⁰
Piperitenone ¹⁰
Oxides
<i>cis</i> -Limonene oxide ^{3,9,18}
<i>trans</i> -Limonene oxide ^{3,9,18}
<i>cis</i> -Linalool oxide ^{3,9,12}
<i>trans</i> -Linalool oxide ^{3,9,12}
Miscellaneous
γ -Decalactone ⁶
1,1-Diehoxyethane ⁷
Diethyl carbonate ¹⁰
1,1-Ethoxymethoxyethane ¹⁰
Ethyl sec-butyl ether ¹³
Hydrogen sulfide ²
Methyl chloride ^{b,13}
Brackets indicate common name
possibly an artifact
1 Attaway <i>et al.</i> (1964)
2 Kirchner and Miller (1967)
3 Wolford and Attaway (1967)
4 Attaway and Wolford (1965)
5 Hall and Wilson (1925)
6 Schultz <i>et al.</i> (1967)
7 Schultz <i>et al.</i> (1971)
8 Wolford <i>et al.</i> (1962)
9 Wolford <i>et al.</i> (1965)
10 Moshonas and Shaw (1973)
11 Wolford <i>et al.</i> (1963)
12 Moshonas <i>et al.</i> (1972)
13 Schultz <i>et al.</i> (1964)
14 Rymal <i>et al.</i> (1968)
15 Askar <i>et al.</i> (1973)
16 Attaway <i>et al.</i> (1962)
17 Dinsmore and Nagy (1971)
18 Shaw and Moshonas (1974)
19 Braddock and Petrus (1971A, B)

conditions were used for their detection. These acids were detected by gas chromatographic analysis after separation from the neutral constituents by steam distillation of essence, first at pH 9.0 and then at pH 1.0 (Attaway *et al.* 1964; Attaway and Wolford 1965). These ten acids were identified by gas chromatography without prior separation from neutral constituents by use of a capillary column and an electron capture detector (Wolford and Attaway 1967).

Alcohols form the largest class of compounds found in orange essence with some 36 having been identified. In one study carbonyl compounds were removed by derivatization prior to gas chromatographic separation of the alcohols (Attaway *et al.* 1964), but most studies were carried out without preliminary carbonyl removal.

Every primary straight-chain alcohol from methanol to decanol has been identified, with ethanol as the main organic constituent of essence. Many terpene alcohols that have been found in cold-pressed orange oil (Hunter and Moshonas 1965) have been found in orange essence also.

Twenty-two aldehydes have been identified as orange essence components. With the exception of the C-5 and C-7 aldehydes, all of the straight-chain saturated aldehydes from acetaldehyde to undecanal have been found. However, the α,β -unsaturated C-5 aldehyde, *trans*-2-pentenal, has been identified in essence, as well as 2-hexenal and 2-octenal. 3-Ethoxyhexanal, found in concentrated orange essence, is formally an addition product of 2-hexenal and the main organic essence component, ethanol. Two aromatic aldehydes, benzaldehyde and furfural have been found in essence, but not in the same studies. Furfural in orange juice has recently been shown to indicate storage abuse (Nagy and Randall 1973). Malonaldehyde was found in only one study and was isolated as a thiobarbituric acid complex (Brad-dock and Petrus 1971A,B).

Twenty-five esters have been reported as essence constituents, with ethyl acetate, ethyl butyrate and ethyl octanoate being those most often found. Most reported esters are those of straight- or branched-chain acids and alcohols. Five terpene esters have been identified as well as methyl *N*-methyl-anthranilate. Both methyl- and ethyl-3-hydroxy-hexanoate have been found in orange essence. They are related chemically to another essence constituent, 3-ethoxyhexanal, discussed previously.

Hydrocarbons, which comprise over 95% of orange oil by weight, are minor components of orange essence. Twenty-seven hydrocarbons have been identified in orange essence, including 15 terpenes, 2 of which are the major orange oil terpenes *d*-limonene and myrcene (Shaw and Coleman 1974). The remaining 12 of the hydrocarbons reported are listed as possible artifacts, introduced either in solvents used to apply resin to the fruit or, in one case (biphenyl), as a fungistat (Schultz *et al.* 1964).

Of the 11 ketones identified in orange essence, 7 are straight-chain ketones, 1 (4-methyl-2-pentanone) is a branch-chain ketone, 1 is a sesquiterpene ketone (nootkatone) and 2 are monoterpene ketones. One of the latter, carvone, occurs naturally in orange as 1-carvone (Shaw and Coleman 1971), whereas, *dl*-carvone is a product of auto-oxidation of *d*-limonene (Schenck *et al.* 1965). The four oxides identified in orange essence are the *cis* and *trans* isomers of limonene and linalool oxides. All four were reported in two studies, and only the linalool oxides were found in a third study.

Under a miscellaneous category in Table 12.1 seven compounds are listed. Two of these are the acetals 1,1-diethoxyethane and 1,1-ethoxymethoxyethane. Moshonas and Shaw (1973) have suggested that 1,1-ethoxymethoxyethane could be formed from 1,1-diethoxyethane and methanol in an acidic juice medium. The one halogenated compound, methyl chloride, is probably an artifact (Schultz *et al.* 1964).

Hydrogen sulfide was the only sulfur-containing compound positively identified as a constituent of orange essence. Wolford and Attaway (1967) treated essence with mercuric chloride to complex volatile sulfur compounds, but were unable to regenerate the sulfur compounds for subsequent analysis. The mercuric chloride treatment did remove most of the orange aroma as well, indicating possible importance of some unidentified volatile sulfur compounds to orange essence flavor.

Quantitative Composition

Quantitative compositional studies on aqueous orange essence have been largely confined to classes of compounds. These quantitative measurements have been used to try to predict strength and flavor quality of essence. Perhaps the most widely used analytical procedure for measuring essence strength is the chemical oxygen demand (COD) method (McNary *et al.* 1957; Dougherty 1964). Since this method measures total oxidizable organic constituents, the main organic component, ethanol, contributes heavily to the COD value. Ethanol is not an important contributor to essence flavor, so a COD value tells little about the strength or flavor quality of an essence (Wolford *et al.* 1969). Attaway *et al.* (1967) reported methods for determining oxygenated terpene, aldehyde and ester concentrations in essences. At the same laboratory a colorimetric method was developed for determining total aldehydes in essence. The method includes the use of *N*-hydroxybenzenesulfonamide to form the colored derivative and *n*-octanal-*trans*-2-hexenal as a mixed standard (Ismail and Wolford 1970; Petrus *et al.* 1970). Wolford *et al.* (1969) described attempts to use measurements from the above methods to predict strength as an index of flavor quality and found the oxygenated terpene-to-octanal ratio and total aldehyde contents to show the most promise.

Several other methods have been developed more recently for estimation of essence strength. Peleg and Mannheim (1970) found that the saturated aldehyde method of Attaway *et al.* (1967) was time-sensitive. Thus end points were difficult to determine. Instead they developed a colorimetric method based on the formation of dinitro-